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Carbonaceous materials for use in the production of aluminium — Green and calcined coke — Determination of trace elements by flame atomic absorption spectroscopy

Produits carbonés utilisés pour la production de l'aluminium — Coke cru et calciné — Détermination des éléments-traces par spectrométrie d'absorption atomique dans la flamme

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 8658 was prepared by the British Standards Institution (BSI) (as BS 6043: Part 2: Section 2.3:1989) and was adopted, under a special "fast-track procedure", by Technical Committee ISO/TC 47, *Chemistry* in parallel with its approval by the ISO member bodies.

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Carbonaceous materials for use in the production of aluminium — Green and calcined coke — Determination of trace elements by flame atomic absorption spectroscopy

1 Scope

This International Standard describes a method for the determination of trace elements in green and calcined coke with an ash content of not greater than 1 % (m/m) and with individual concentrations not greater than the following:

Calcium	0,025 % (m/m)
Chromium	0,005 % (m/m)
Copper	0,025 % (m/m)
Iron	0,030 % (m/m)
Lead	0,010 % (m/m)
Magnesium	0,010 % (m/m)
Manganese	0,001 % (m/m)
Nickel	0,050 % (m/m)
Silicon	0,100 % (m/m)
Vanadium	0,100 % (m/m)
Zinc	0,004 % (m/m)

NOTE — A method for the determination of ash of cokes is given in ISO 8005:1984, *Carbonaceous materials used in the production of aluminium — Green and calcined coke — Determination of ash*. However, it is essential that the ash produced by that method not be used in the procedure of this International Standard because of the risk of contamination by trace elements.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 835-1:1981, *Laboratory glassware — Graduated pipettes — Part 1: General requirements.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for laboratory use — Specification and test methods.*

ISO 6375:1980, *Carbonaceous materials for the production of aluminium — Coke for electrodes — Sampling.*

3 Principle

A test portion sample is heated in a muffle furnace at 700 °C for 10 h and the ash produced is fused with a mixture of sodium carbonate and orthoboric acid. The melt is dissolved in dilute hydrochloric acid and the trace metal content is analysed by flame atomic absorption spectrometry.

4 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade and water complying with grade 2 of ISO 3696.

4.1 Sodium carbonate, anhydrous.

4.2 Orthoboric acid.

4.3 Hydrochloric acid, concentrated, $c(\mathrm{HCl}) = 36\ \%\ (m/m)$, $\rho = 1{,}16$ g/ml.

4.4 Lanthanum chloride solution, 100 mg La/ml, atomic absorption grade, $c(\mathrm{LaCl_3 \cdot 7H_2O}) = 267$ g/l.

4.5 Standard calcium solution, 0,1 mg/Cal.

Dry calcium carbonate (reagent grade) at 110 °C ± 5 °C for 1 h and cool in a desiccator containing diphosphorus pentoxide. Weigh 2,497 g ± 0,001 g into a 250 ml beaker. Add 50 ml of water, then, a little at a time, 50 ml of concentrated hydrochloric acid (4.3). When the solution is clear, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

Using a one-mark pipette (5.8), transfer 10 ml of this solution to a 100 ml one-mark volumetric flask (5.6). Add approximately 20 ml of water and 5 ml of hydrochloric acid (4.3). Dilute to the mark with water and mix.

4.6 Standard chromium solution, 0,1 mg Cr/ml.

Wash, by decantation, approximately 1,2 g of chromium metal of minimum purity 99,9 % (m/m) with dilute hydrochloric acid [$c(\mathrm{HCl}) = 1$ mol/l], then wash with water and dry in an air-circulating oven maintained at 110 °C ± 5 °C for 10 min. Weigh 1 g ± 0,001 g of the dried chromium into a 250 ml beaker containing about 50 ml of water. Slowly add 50 ml of concentrated hydrochloric acid (4.3). After dissolution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

Using a one-mark pipette (5.8), transfer 10 ml of this solution to a 100 ml one-mark volumetric flask (5.6). Add approximately 20 ml of water and 5 ml of concentrated hydrochloric acid. Dilute to the mark with water and mix. Store in a polythene bottle.

4.7 Standard copper solution, 1 mg Cu/ml.

Wash, by decantation, approximately 1,2 g of copper metal of minimum purity 99,9 % (m/m) with dilute nitric acid [$c(\mathrm{HNO_3}) = 2$ mol/l], then wash with water and dry in an air-circulating oven maintained at 110 °C ± 5 °C for 10 min. Weigh 1 g ± 0,001 g of the dried copper into a 250 ml beaker containing about 25 ml of water. Slowly add 35 ml of concentrated nitric acid ($\rho = 1{,}42$ g/ml). After dissolution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

4.8 Standard iron solution, 1 mg Fe/ml.

Weigh 1 g ± 0,001 g of iron of minimum purity 99,9 % (m/m) into a 250 ml beaker and add 25 ml of water. Carefully add 50 ml of concentrated hydrochloric acid (4.3). After dissolution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

4.9 Standard magnesium solution, 0,01 mg Mg/ml.

Weigh 1 g ± 0,001 g of magnesium of minimum purity 99,9 % (*m*/*m*) into a 250 ml beaker and add 50 ml of water. Carefully add 50 ml of concentrated hydrochloric acid (4.3). After dissolution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

Using a one-mark pipette (5.8), transfer 10 ml of this solution to a 1 000 ml one-mark volumetric flask (5.6). Add approximately 50 ml of water and 45 ml of concentrated hydrochloric acid (4.3). Dilute to the mark with water and mix.

4.10 Standard manganese solution, 0,1 mg Mn/ml.

Wash, by decantation, approximately 1,2 g of manganese metal of minimum purity 99,9 % (*m*/*m*) with dilute nitric acid [$c(HNO_3)$ = 2 mol/l], then wash with water and dry in an air air-circulating oven maintained at 110 °C ± 5 °C for 10 min. Weigh 1 g ± 0,001 g of the dried manganese into a 250 ml beaker containing about 25 ml of water. Slowly add 35 ml of concentrated nitric acid (ρ = 1,42 g/ml). After dissolution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

Using a one-mark pipette (5.8), transfer 10 ml of this solution to a 100 ml one-mark volumetric flask (5.6). Add approximately 50 ml of water and 3 ml of concentrated nitric acid (ρ = 1,42 g/ml). Dilute to the mark with water and mix.

4.11 Standard nickel solution, 1 mg Ni/ml.

Weigh 1 g ± 0,001 g of nickel of minimum purity 99,9 % (*m*/*m*) into a 250 ml beaker and add 25 ml of water. Carefully add 35 ml of concentrated nitric acid (ρ = 1,42 g/ml), and heat to dissolve. After dissolution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

4.12 Standard lead solution, 1 mg Pb/ml.

Weigh 1 g ± 0,001 g of lead of minimum purity 99,9 % (*m*/*m*) into a 250 ml beaker and add 25 ml of water. Carefully add 35 ml of concentrated nitric acid (ρ = 1,42 g/ml), and heat to dissolve. After dissolution, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6). Dilute to the mark with water and mix. Store in a polythene bottle.

4.13 Standard silicon solution, 1 mg Si/ml.

Into a platinum dish or large platinum crucible, weigh 2,139 g of silica of minimum purity 99,9 % (*m*/*m*) and 6 g of anhydrous sodium carbonate (4.1), and mix well with a platinum spatula. Carefully fuse the mixture over a flame until a transparent melt is obtained. Allow to cool, add warm water, heat gently until completely dissolved and transfer quantitatively to a 400 ml PTFE beaker. Allow to cool. Dilute the solution to about 300 ml with water, transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.6), dilute to the mark with water and mix. Immediately transfer this solution to a screw-cap polythene bottle.

Discard this solution after one month.

4.14 Standard vanadium solution, 1 mg V/ml.

Heat vanadium(V) oxide of minimum purity 99,9 % (*m*/*m*) in a covered platinum crucible (5.9) at 500 °C ± 10 °C for 30 min and cool in a desiccator. Weigh 1,785 g of the dried material and dissolve in a slight excess of sodium hydroxide solution [$c(NaOH)$ = 1 mol/l] in a PTFE beaker, then dilute to about 250 ml with water. Carefully add, a little at a time, concentrated sulfuric acid [$c(0,5\ H_2SO_4)$ = 9 mol/l], until the solution is just acid to litmus paper, then add a further 5 ml. Cool to room temperature, transfer to a 1 000 ml one-mark volumetric flask (5.6), dilute to the mark with water and mix.

4.15 Standard zinc solution, 0,1 mg Zn/ml.

Weigh 1 g ± 0,001 g of zinc of minimum purity 99,9 % (*m*/*m*) into a 100 ml beaker and add 25 ml of water. Carefully add 25 ml of concentrated hydrochloric acid (4.3) and heat to dissolve. After dissolution, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask (5.6), dilute to the mark with water and mix.

Using a one-mark pipette (5.8), transfer 10 ml of this solution to a 100 ml one-mark volumetric flask (5.6), add about 20 ml water and 5 ml of concentrated hydrochloric acid (4.3). Dilute to the mark with water and mix.

5 Apparatus

Ordinary laboratory apparatus and the following are required. All glass and plastics apparatus shall be cleaned before use by washing in concentrated hydrochloric acid (4.3) and rinsing with water (see clause 4, introductory paragraph).

5.1 Spectrometer, atomic absorption type, fitted with a burner fed from cylinders of acetylene, dinitrogen oxide (nitrous oxide) and compressed air. The emission wavelength and slit width shall be variable.

5.2 Electric muffle furnace, capable of being maintained at 700 °C ± 10 °C.

5.3 Meker burner.

5.4 Sieve, with a polythene frame and polyester mesh having an aperture size in the range 500 µm to 1 000 µm.

5.5 Pestle and mortar, made from sintered alumina or from ferrous metal with a tungsten carbide liner.

NOTE — Pestles and mortars made from other materials are not suitable.

5.6 One-mark volumetric flasks, complying with ISO 1042, class A.

5.7 Burettes, 25 ml, complying with ISO 385-1, class A.

5.8 One-mark pipettes, complying with ISO 835-1, class A.

5.9 Platinum crucibles, with covers, 40 ml capacity.

To clean, place about 2,5 g of anhydrous sodium carbonate (4.1) and 1 g of orthoboric acid (4.2) into each crucible and mix. Replace the covers, then fuse the mixture over a Meker burner (5.3). Cool, dissolve the solidified melt in concentrated hydrochloric acid (4.3) and rinse with water (see clause 4, introductory paragraph). Dry in an oven at 110 °C ± 5 °C and cool in a desiccator.

5.10 Platinum rod or spatula.

6 Sampling

Prepare a crushed representative sample in accordance with ISO 6375, ensuring that the milling procedure utilizes a jaw crusher faced with tungsten carbide and a 5 mm aperture sieve with a polythene frame and a polyester mesh (see ISO 6375).

7 Procedure

7.1 Preparation of the test sample

Thoroughly mix the crushed sample (see clause 6) and reduce it by coning and quartering to at most 50 g. Grind the reduced sample with the pestle and mortar (5.5) to a fineness such that all the material passes through the sieve (5.4). Mix well.

7.2 Test portion

Weigh 5 g ± 0,001 g of the test sample into a tared platinum crucible (5.9). Place the crucible, without cover, in the cold muffle furnace (5.2). Raise the furnace temperature gradually and maintain it at 700 °C ± 10 °C for 10 h. Remove the crucible and ash, allow it to cool in a desiccator and weigh as rapidly as possible. Return the crucible and ash to the furnace for 2 h and continue the cycle of heating, cooling and weighing until successive masses differ by no more than 1 mg.

7.3 Preparation of calibration solutions

7.3.1 Calibration solutions A

To each of four 600 ml beakers, add 25 g ± 0,1 g of anhydrous sodium carbonate (4.1) and 10 g ± 0,1 g of orthoboric acid (4.2) and 300 ml of water. Mix well. Cautiously add 90 ml of concentrated hydrochloric acid (4.3). Once dissolved, transfer quantitatively the contents of each beaker to one of four 1 000 ml one-mark volumetric flasks (5.6), labelled A1, A2, A3 and A4. Using clean one-mark pipettes (5.8), add the volume shown in table 1 of each standard solution to the corresponding flask. Dilute each solution to the mark with water and mix.

NOTES

1 The standard silica solution should be added carefully, with swirling, to avoid the possibility of precipitation.

2 The concentrations of the relevant elements are given in table 2.

Table 1 — Composition of calibration solutions A

Calibration solution	Volumes of standard solutions ml								
	Cr (4.6) 0,1 mg/ml	Cu (4.7) 1 mg/ml	Fe (4.8) 1 mg/ml	Mn (4.10) 0,1 mg/ml	Ni (4.11) 1 mg/ml	Pb (4.12) 1 mg/ml	Si (4.13) 1 mg/ml	V (4.14) 1 mg/ml	Zn (4.15) 0,1 mg/ml
A1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
A2	10,0	10,0	10,0	2,0	10,0	2,0	25,0	25,0	10,0
A3	30,0	15,0	20,0	5,0	30,0	5,0	50,0	50,0	20,0
A4	50,0	25,0	30,0	10,0	50,0	10,0	100,0	100,0	40,0

Table 2 — Concentrations of elements in calibration solutions A

Calibration solution	Concentration µg/ml								
	Cr	Cu	Fe	Mn	Ni	Pb	Si	V	Zn
A1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
A2	1,0	10,0	10,0	0,2	10,0	2,0	25,0	25,0	1,0
A3	3,0	15,0	20,0	0,5	30,0	5,0	50,0	50,0	2,0
A4	5,0	25,0	30,0	1,0	50,0	10,0	100,0	100,0	4,0

7.3.2 Calibration solutions B

To a 100 ml beaker, add 2,5 g ± 0,1 g of anhydrous sodium carbonate (4.1), 1 g ± 0,1 g of orthoboric acid (4.2) and 30 ml of water. Cautiously add 10 ml of concentrated hydrochloric acid (4.3). Once dissolved, transfer quantitatively to a 100 ml one-mark volumetric flask (5.6), dilute to the mark with water and mix. Transfer, using a burette (5.7), 20 ml portions of this solution to each of four 100 ml one-mark volumetric flasks (5.6) labelled B1, B2, B3 and B4. To each flask, add 10,00 ml of lanthanum chloride solution (4.4) from a burette (5.7) and 4,5 ml of concentrated hydrochloric acid (4.3). Using clean one-mark pipettes (5.8), add the volume shown in table 3 of each standard solution to the corresponding flask. Dilute each solution to the mark with water and mix.

Table 3 — Composition of calibration solutions B

Calibration solution	Volume of standard calcium solution (4.5) ml	Concentration of calcium µg/ml	Volume of standard magnesium solution (4.9) ml	Concentration of magnesium µg/ml
B1	0,0	0,0	0,0	0,0
B2	1,0	1,0	5,0	0,5
B3	3,0	3,0	10,0	1,0
B4	5,0	5,0	20,0	2,0

7.4 Determination

7.4.1 Preparation of test solution A

To the crucible containing the ashed test portion (see 7.2) add 1,25 g ± 0,01 g of anhydrous sodium carbonate (4.1) and 0,5 g ± 0,01 g of orthoboric acid (4.2). Mix with the platinum rod or spatula (5.10). Cover the crucible and fuse the ash using the Meker burner (5.3) for 14 to 15 min. Allow to cool.

Add 15 ml of water to the crucible and heat gently to partially dissolve the solidified melt. Transfer quantitatively the contents of the crucible to a 100 ml beaker by rinsing the crucible and cover with 10 ml of warm water followed by 6 ml of concentrated hydrochloric acid (4.3). Maintain gentle heating. When the solution becomes clear, allow it to cool to room temperature, transfer quantitatively to a 50 ml one-mark volumetric flask (5.6), dilute to the mark with water and mix.

7.4.2 Preparation of test solution B

Using a pipette (5.8), transfer 5 ml of test solution A into a 25 ml one-mark volumetric flask (5.6). From a burette (5.7), add 2,5 ml of lanthanum chloride solution (4.4) and 1,0 ml of concentrated hydrochloric acid (4.3), dilute to the mark with water and mix.

7.4.3 Preparation of reagent blanks A and B

Follow the procedures described in 7.4.1 and 7.4.2, respectively, omitting the test portion (see 7.2).

7.4.4 Spectrometric measurements

7.4.4.1 Preparation for the measurement of each element

Install in the spectrometer (5.1) the appropriate hollow-cathode lamp, adjust the lamp current in accordance with the manufacturer's recommendations and allow the instrument to stabilize for 10 min. Select the slit width and wavelength in accordance with table 4. Fit the burner head corresponding to the flame type given in table 4 and ignite in accordance with the manufacturer's instructions. While aspirating a solution containing the element to be measured, optimize the burner head position, the flame condition and the nebulizer efficiency.

Set the read-out integration time to at least 5 s; if the instrument possesses a microprocessor capable of multiple readings, set for four 5 s readings with an average and standard deviation print-out. Aspirate water and zero the absorption read-out.

Table 4 — Conditions for spectrophotometric measurements

Element	Flame	Wavelength nm	Slit width nm
Ca	dinitrogen oxide/acetylene (reducing, red)	422,7	0,7
Cr	air/acetylene (reducing, rich, yellow)	357,9	0,7
Cu	air/acetylene (oxidizing, lean, blue)	324,8	0,7
Fe	air/acetylene (oxidizing, lean, blue)	248,3	0,2
Mg	air/acetylene (oxidizing, lean, blue)	285,2	0,7
Mn	air/acetylene (oxidizing, lean, blue)	279,5	0,2
Ni	air/acetylene (oxidizing, lean, blue)	232,0	0,2
Pb	air/acetylene (oxidizing, lean, blue)	283,3	0,7
Si	dinitrogen oxide/acetylene (reducing, rich, red)	251,6	0,2
V	dinitrogen oxide/acetylene (reducing, rich, red)	318,4	0,7
Zn	air/acetylene (oxidizing, lean, blue)	213,9	0,7

7.4.4.2 Measurement

For each element to be analysed, prepare the instrument as described in 7.4.4.1. Complete all measurements relevant to each element before altering the instrument settings.

Interpose the corresponding sample, calibration and blank solutions (e.g. test solution A with calibration solutions A1 to A4) in a random sequence at regular time intervals and read all of the solutions twice, in reverse order on the second occasion to compensate for drift. Calculate the mean of the duplicate readings for each of the solutions.

8 Calculation and expression of results

8.1 Calibration curve

For each element analysed, correct the mean absorbance values of the appropriate calibration solutions A2 to A4 or B2 to B4 by subtracting the absorbance values of the appropriate calibration solution A1 or B1. Prepare a calibration curve by plotting the corrected absorbance against the concentration of the element in micrograms per litre.

8.2 Calculation

For each element analysed, subtract the absorbance of the appropriate reagent blank A or B from the absorbance of the test solution A or B. Using the corrected absorbance value and the calibration curve obtained for the same element, obtain the corresponding concentration value.

Calculate the content of each element, as a percentage by mass in the test sample, from the following equations: